

Title:**Catalyst system comprising magnesium halide**

The present invention relates to a catalyst system comprising a single site catalyst component containing a transition metal, supported on an adduct containing magnesium halide, and an organoaluminum compound.

Single site catalyst components are well known in the art and are usually used in conjunction with alumoxanes or boron compounds as cocatalysts in polymerization processes. The catalyst systems so obtained can be used supported on an inert support in order to control the morphology of the obtained polymer and to avoid fouling in the reactor, especially in a gas-phase or slurry polymerization processes.

The drawback of the catalyst systems so obtained is that since alumoxanes need to be used in large excess with respect to the single site catalyst components, the resulting catalyst is very expensive. Therefore it is desirable to reduce or eliminate the use of alumoxanes.

When boron compounds are used as cocatalyst, a large excess is not required. However they have the drawback of being more expensive than alumoxanes and dangerous to handle.

Magnesium chloride is a well-known support for classic Ziegler Natta catalyst systems based on $TiCl_4$ or $TiCl_3$. The use of this compound as a carrier for single-site catalysts could be very advantageous, in view of its chemical and structural simplicity, and the possibility to finely control the porosity of this support and, therefore, to easily tune the porosity of the final catalyst system.

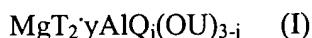
Adducts containing magnesium chloride and an organoaluminum compound have already been proposed as supports for metallocene-based catalyst components in which the central atom is zirconium, titanium or hafnium. For example, in Macromol. Chem. Phys. 195, 1369-1379 (1984), $MgCl_2$ in combination with a zirconocene catalyst and trialkylaluminum is used. More recently, In Macromolecules 1993, 26, 4712, mixtures of MgR_2 and AlR_2Cl (generating $MgCl_2$ and AlR_3) as cocatalyst components for olefin polymerization using various metallocenes have been used. In various papers, namely, Korean J. Chem. Eng. 16(5) 562-570, Journal of Applied Polymer science Vol 70, 1707-1715, Korean J. Chem. Eng. 19(4) 557-563 and J. Molec. Catal A 191, 2003, 155-165, Lee and co-workers proposed a metallocene-based catalyst system in which alcohol and anhydrous $MgCl_2$ are reacted to form an adduct $MgCl_2$ -alcohol. The adduct, further reacted

with trialkylaluminum, is used for supporting zirconocene compounds. The obtained catalyst system can be used without a further addition of alumoxanes.

However, there is still the need to find alternative, easily obtainable supports for other kinds of single site catalyst system allowing elimination of the use of alumoxanes or boron compounds.

An object of the present invention is therefore a supported catalyst system comprising the product obtainable by contacting:

- a) an adduct of formula (I)



wherein

Mg is magnesium; Al is aluminum; O is oxygen;

T is chlorine, bromine, or iodine, preferably chlorine;

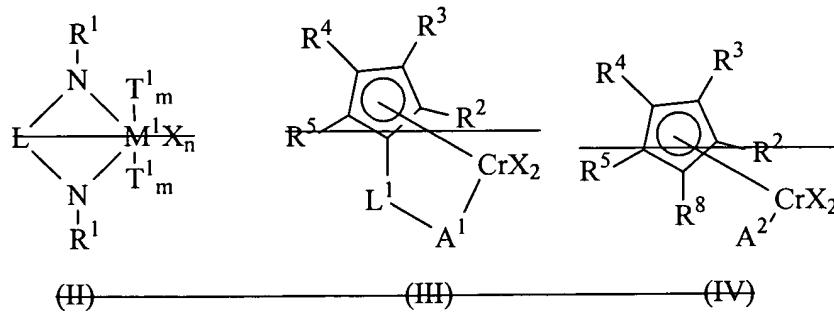
U is a linear or branched C₁-C₁₀ alkyl radical, preferably U is a linear C₁-C₁₀ alkyl radical; more preferably U is a methyl or an ethyl radical;

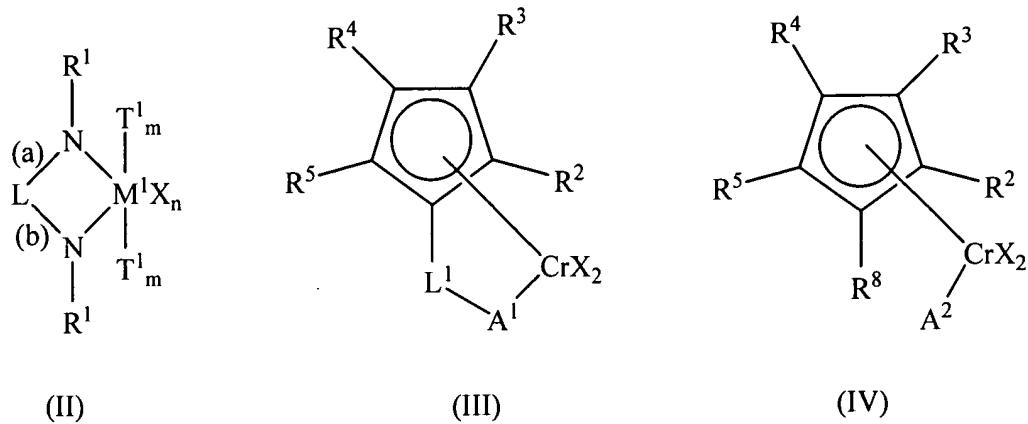
y ranges from 6.00 to 0.05; preferably y ranges from 2 to 0.1, more preferably from 1 to 0.1;

j ranges from 3 to 0.1, preferably from 3 to 0.5; more preferably from 3 to 1 being also a non integer number;

Q substituent, same or different, is a hydrocarbon radical containing from 1 to 20 carbon atoms optionally containing silicon or germanium atoms; preferably Q is a linear or branched, cyclic or acyclic, C₁-C₂₀-alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl or C₇-C₂₀-arylalkyl radicals optionally containing silicon or germanium atoms; more preferably Q is a linear or branched C₁-C₂₀-alkyl radical; even more preferably Q is an ethyl, a n-propyl, an iso-propyl, a n-butyl, an iso-butyl, a tert-butyl, a hexyl or an octyl radical;

- b) with at least one compound selected from the compounds of formula (II), (III) and (IV)





wherein:

in the compound of formula (II):

M¹ is a transition metal atom selected from Groups 3-11 of Periodical Table (Group 3 including lanthanoids); preferably M¹ is a transition metal atom selected from Groups 3-6 and 8-10, more preferably M¹ is a transition metal atom selected from Groups 4, 5, and 6; still more preferably M¹ is a metal of Group 4 or 5: specifically including scandium, titanium, zirconium, hafnium, vanadium, niobium, tantalum, cobalt, rhodium, yttrium, chromium, molybdenum, tungsten, manganese, rhenium, iron, ruthenium, nickel, and palladium; preferably scandium, titanium, zirconium, hafnium, vanadium, niobium, tantalum, iron, cobalt, rhodium, nickel, and palladium; more preferably titanium, zirconium, hafnium, vanadium, nickel, niobium, tantalum, chromium, and molybdenum; still more preferably titanium, vanadium and nickel; the substituents X, equal to or different from each other, are monoanionic sigma ligands selected from the group consisting of hydrogen, halogen, R, OR, OCOR, SR, NR₂ and PR₂, wherein R is a hydrocarbon radical containing from 1 to 20 carbon atoms, optionally containing one or more Si or Ge atoms; preferably X is an halogen atom or a R group; more preferably X is chlorine or a C₁-C₁₀ alkyl radical, such as a methyl or an ethyl radical;

n ranges from 0 to 3; preferably n is 2;

[[the]] bonds (a) and (b) connecting the two nitrogen atoms with the bridge L, same or different, can be a single bond or double bond or double bonds;

L is a divalent or trivalent bridge connecting the two nitrogen atoms; preferably L is a divalent or trivalent C₁-C₄₀ hydrocarbon group, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements;

each R¹, equal to or different from each other, is a C₁-C₄₀ hydrocarbon radical optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; preferably R¹ is a hydrogen atom, or a linear or branched, cyclic or acyclic, C₁-C₂₀-alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl or C₇-C₂₀-arylalkyl radical optionally containing silicon atoms;

m ranges from 0 to 1; when m is 0 the group T¹ is not-existent;

T¹ is a Lewis base, such as tetrahydrofuran, tertiary amine, pyridine, pyrrole and the like. The group T¹ can also be bonded to the group R¹;

in the compound of formula (III):

Cr is a chromium atom; X is as described above;

each R², R³, R⁴ and R⁵, equal to or different from each other, is a hydrogen atom, a halogen atom, or a C₁-C₄₀ hydrocarbon radical optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; or two adjacent R², R³, R⁴ and R⁵ form one or more C₃-C₇ membered ring optionally containing heteroatoms belonging to groups 13-17 of the periodic table; preferably each R², R³, R⁴ and R⁵, equal to or different from each other, is a hydrogen atom, halogen atom or a linear or branched, cyclic or acyclic, C₁-C₂₀-alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl or C₇-C₂₀-arylalkyl radical; or two adjacent R², R³, R⁴ and R⁵ can form one or more C₃-C₇ membered ring;

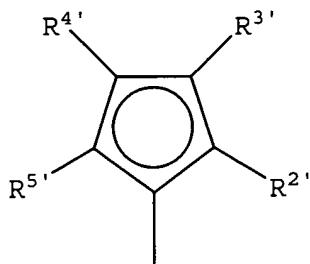
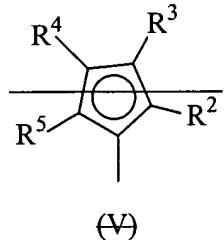
L¹ is a divalent bridging group selected from a C₁-C₂₀ alkylidene, a C₃-C₂₀ cycloalkylidene, a C₆-C₂₀ arylidene, a C₇-C₂₀ alkylarylidene, or a C₇-C₂₀ arylalkylidene radical optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements, and a silylidene radical containing up to 5 silicon atoms such as SiMe₂, SiPh₂; preferably L¹ is a divalent group (ZR⁶)_{n1}; Z being C, Si, Ge, N or P, and each R⁶ group, equal to or different from each other, is a hydrogen atom or a hydrocarbon group containing from 1 to 20 carbon atoms, or two R⁶ can form an aliphatic or aromatic C₄-C₇ ring; preferably R⁶ is a hydrogen atom or a linear or branched, cyclic or acyclic, C₁-C₂₀-alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl or C₇-C₂₀-arylalkyl radical;

more preferably L¹ is selected from Si(CH₃)₂, SiPh₂, SiPhMe, SiMe(SiMe₃), CH₂, (CH₂)₂, (CH₂)₃ or C(CH₃)₂;

m1 is 1 or 2, and more specifically m1 is 1 when Z is N or P, and m1 is 2 when Z is C, Si or Ge;

n1 is an integer ranging from 1 to 4; preferably n1 is 1 or 2;

A¹ is a moiety of formula (V)



(V)

wherein R², R³, R⁴ and R⁵ are as described above R^{2'}, R^{3'}, R^{4'} and R^{5'} are hydrogen, halogen, or C₁-C₄₀ hydrocarbon radicals optionally comprising one or more heteroatoms belonging to groups 13-17 of the Periodic Table of Elements; or two adjacent R², R³, R⁴ and R⁵ form at least one C₃-C₇ membered ring optional comprising at least one heteroatom belonging to groups 13-17 of the Periodic Table of Elements; or A¹ is an oxygen atom, a sulphur atom, a NR⁷, NR⁷₂, a OR⁷ or a SR⁷ group, wherein R⁷ is a C₁-C₄₀ hydrocarbon radical, preferably R⁷ is a linear or branched, cyclic or acyclic, C₁-C₂₀-alkyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl or C₇-C₂₀-arylalkyl radical; more preferably R⁷ is a C₁-C₂₀-alkyl radical, such as a methyl or an ethyl radical; preferably A¹ is a NR⁷₂ group;

in the compound of formula (IV):

Cr is chromium; X, R², R³, R⁴ and R⁵ are as described above, and R⁸ has the same meaning given for R², R³, R⁴ and R⁵;

A² is halogen, R⁷, OR⁷, OCOR⁷, SR⁷, NR⁷₂, NR⁷₃, SR⁷₂, OR⁷₂ wherein R⁷ is a C₁ – C₄₀ hydrocarbon radical; preferably A² is a NR⁷₃ group A² is halogen, R⁷, OR⁷, OCOR⁷, SR⁷, NR⁷₂, NR⁷₃, SR⁷₂, OR⁷₂ wherein R⁷ is as described above; preferably A² is a NR⁷₃ group.

The adduct of formula (I)



generally has a surface area (BET) higher than 30 m²/g; more preferably higher than 38 m²/g; even more preferably higher than 200 m²/g; but it can reach values higher than 300 m²/g. It can be obtained with methods commonly known in the art. For example the adduct MgT₂wUOH, wherein w ranges from 0.1 to 6, is contacted with an aluminum compound of formula H_eAlQ¹_{3-e} or H_eAl₂Q¹_{6-e}, in an inert solvent; where each Q¹ substituent, same or different, is hydrogen atom, halogen atom, or a hydrocarbon radical containing from 1 to 20 carbon atoms optionally containing silicon or germanium atoms; with the proviso that at least one Q¹ is different from halogen, and e ranges from 0 to 1, being also a non-integer number; preferably said hydrocarbon radicals is a linear or branched, cyclic or acyclic, C₁-C₂₀-alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl or C₇-C₂₀-arylalkyl radical optionally containing silicon or germanium atoms; preferably Q¹ is a linear or branched C₁-C₂₀-alkyl radical; more preferably Q¹ is an ethyl, a n-propyl, an iso-propyl, a n-butyl, an iso-butyl, a tert-butyl, a hexyl or an octyl radical. Examples of this reaction can be found in US 4,399,054 and US 5,698,487.

Preferably the adduct of formula MgT₂wUOH MgT₂wUOH is partially dealcoholated as described in US 5,698,487. Therefore a further object of the present invention is a supported catalyst system obtainable by the process comprising the following steps:

a) contacting

- (i) a partially dealcoholated adduct of formula MgT₂wUOH MgT₂wUOH wherein [T] T' is chlorine, bromine, or iodine, preferably chlorine; U is a linear or branched C₁-C₁₀ alkyl radical, preferably U is a linear C₁-C₁₀ alkyl radical; more preferably U is a methyl or an ethyl radical; w ranges from 6 to 0.1, preferably from 3 to 0.5; more preferably from 2.9 to 0.5 being also a non integer number; with
- (ii) an organo-aluminium compound of formula H_eAlQ¹_{3-e} or H_eAl₂Q¹_{6-e}, wherein each Q¹ substituent, same or different, is a hydrogen atom, a halogen atom, or a hydrocarbon radical containing from 1 to 20 carbon atoms optionally containing

silicon or germanium atoms; with the proviso that at least one Q¹ is different from halogen, and e ranges from 0 to 1, being also a non-integer number; preferably said hydrocarbon radical is a linear or branched, cyclic or acyclic, C₁-C₂₀-alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl or C₇-C₂₀-arylalkyl radical optionally containing silicon or germanium atoms; preferably Q¹ is a linear or branched C₁-C₂₀-alkyl radical; more preferably Q¹ is an ethyl, a n-propyl, an iso-propyl, a n-butyl, an iso-butyl, a tert-butyl, a hexyl or an octyl radical;

to obtain an adduct of formula (I) MgT₂^yAlQ_j(OU)_{3-j} described above; and

- b) contacting the product obtained from step a) with at least one compound selected from the compounds of formula (II), (III) and (IV) as described above.

The partially dealcoholated adduct of formula MgT₂wUOH MgT'₂wUOH used in step a) can be obtained by partial dealcoholation of adducts of MgT₂ MgT'₂ with alcohols, said adducts contains from 1 to 6 mol of alcohol. It is possible that two adducts having the same content of alcohol, i.e. having the same empirical formula, are different in porosity and surface area for the reason that one adduct is partially dealcoholated.

The dealcoholation can be carried out according to known methodologies such as those described in US 5,698,487. Depending on the extent of the dealcoholation treatment, partially dealcoholated adducts can be obtained having an alcohol content generally ranging from 0.1 to 3 moles of alcohol per mole of MgT₂ MgT'₂, preferably from 2.9 to 0.5; more preferably from 2.9 to 1.

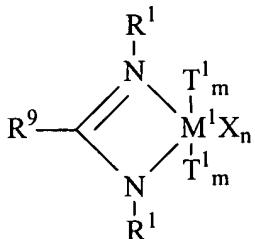
Said partially dehalcoholated magnesium adduct is then contacted with an organo-aluminium compound of formula H_eAlQ¹_{3-e} or H_eAl₂Q¹_{6-e} in an inert solvent with methods common known in the art, such as the method described in EP-A-553 806.

In step b) of the process of the present invention at least one compound of formula (II), (III), and (IV) can be supported on the carrier obtained in step a) according to known methods by bringing the product of step a) into contact, for example, with a solution of the said compound, operating at temperatures between room temperature and 120°C. The amount of said compound that is not fixed on the support is removed by filtration or similar methods.

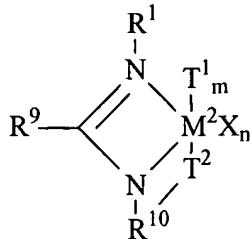
The amount of said compounds supported on the adduct of formula (I) is generally between 1000 µmol/g of support and 1 µmol/g of support; preferably said amount ranges

from 500 $\mu\text{mol/g}$ of support to 2 $\mu\text{mol/g}$ of support; more preferably from 200 $\mu\text{mol/g}$ of support to 2 $\mu\text{mol/g}$ of support.

Preferably, the compound of formula (II) has formulas (IIa) or (IIb)



(IIa)



(IIb)

wherein R¹, T¹, M¹, X, m and n are as described above;

R⁹ is a hydrogen atom or a linear or branched, cyclic or acyclic, C₁-C₂₀-alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl or C₇-C₂₀-arylalkyl radical optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of Elements; preferably R⁹ is a C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl or C₇-C₂₀-arylalkyl radical;

R¹⁰ is a divalent group selected from C₁-C₂₀ alkylidene, C₃-C₂₀ cycloalkylidene, C₆-C₂₀ arylidene, C₇-C₂₀ alkylarylidene, or C₇-C₂₀ arylalkylidene radical optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements, and a silylidene radical containing up to 5 silicon atoms; preferably R¹⁰ is a C₁-C₂₀ alkylidene radical; more preferably it is an ethylidene or a propylidene radical;

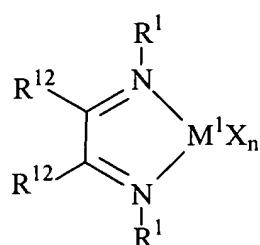
T² is an OR¹¹, SR¹¹ or a NR¹¹₂ radical, wherein R¹¹ is a linear or branched, cyclic or acyclic, C₁-C₁₀-alkyl, C₂-C₁₀ alkenyl, C₂-C₁₀ alkynyl, C₆-C₁₀-aryl, C₇-C₁₀-alkylaryl or C₇-C₁₀-arylalkyl radical;

preferably T¹ is tetrahydrofuran, a tertiary amine, pyridine or pyrrole;

preferably M¹ is titanium or vanadium;

preferably n is 2 and preferably m is 1;

in a further embodiment, the compound of formula (II) has formula (IIc),



(IIc)

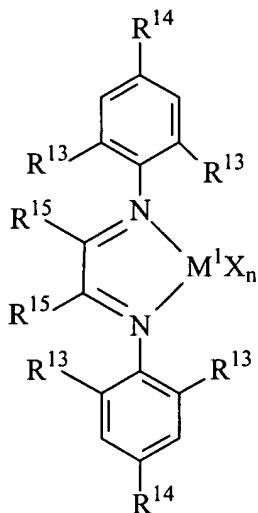
wherein R¹, T¹, M¹, X, and n are as described above;

each R¹², equal to or different from each other, is a hydrogen atom or a linear or branched, cyclic or acyclic, C₁-C₂₀-alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl or C₇-C₂₀-arylalkyl radical optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; two R¹² groups can also join to form a C₃-C₈membered ring that can bear one or more C₁-C₁₅-alkyl, C₂-C₁₅ alkenyl, C₂-C₁₅ alkynyl, C₆-C₁₅-aryl, C₇-C₁₅-alkylaryl or C₇-C₁₅-arylalkyl substituents;

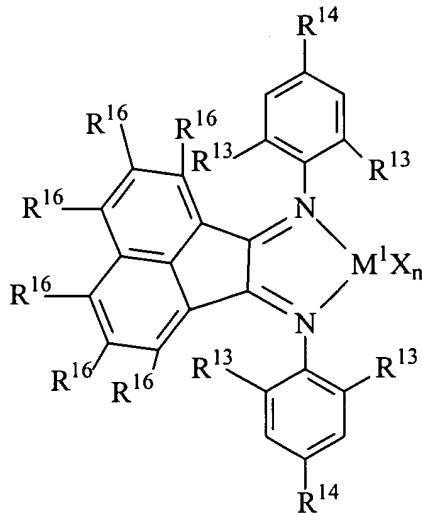
preferably R¹ is a C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl or C₇-C₂₀-arylalkyl radical;

preferably M¹ is nickel and n is 2; X is preferably bromine.

Preferred compounds belonging to formula (IIc) are compounds of formula (IIca) and (IIcb)



(IIIca)



(IIIcb)

wherein:

each R¹³, equal to or different from each other, is a hydrogen atom or a linear or branched, cyclic or acyclic, C₁-C₁₀-alkyl radical, such as methyl, ethyl and isopropyl radicals; preferably R¹³ is a C₁-C₁₀ alkyl radical;

each R¹⁴, equal to or different from each other, is a hydrogen atom or a linear or branched, cyclic or acyclic, C₁-C₁₀-alkyl radical ; preferably R¹⁴ is a hydrogen atom or a C₁-C₁₀ alkyl radical;

R¹⁵, equal to or different from each other, is a hydrogen atom or a linear or branched, cyclic or acyclic, C₁-C₂₀-alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl or C₇-C₂₀-arylalkyl radical optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; preferably R¹⁵, equal to or different from each other, is a hydrogen atom or a linear or branched, cyclic or acyclic, C₁-C₂₀-alkyl radical;

each R¹⁶, equal to or different from each other, is a hydrogen atom or a C₁-C₁₅-alkyl, C₂-C₁₅ alkenyl, C₂-C₁₅ alkynyl, C₆-C₁₅-aryl, C₇-C₁₅-alkylaryl or C₇-C₁₅-arylalkyl radical; preferably R¹⁶ is a hydrogen atom.

Compounds belonging to formulas (II), (III), and (IV) are well known in the art. They are described for example in WO 96/23010, WO 97/02298, WO 98/40374, US 5,707,913 and *Organometallics* 2000, 19, 388.

The catalyst system object of the present invention can be used for (co)polymerizing one or more olefins. Therefore a further object of the present invention is a process for (co)polymerizing olefins containing from 2 to 20 carbon atoms comprising contacting one or more of said olefins under polymerization conditions in the presence of the catalyst system described above. Preferably alpha-olefins containing from 2 to 20 carbon atoms are used.

Examples of alpha-olefins that can be used with the process of the present invention are: ethylene, propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene, 4,6-dimethyl-1-heptene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and 1-eicosene. Preferred olefins are propylene, ethylene 1-butene, 1-hexene and 1-octene.

The catalyst system object of the present invention are particularly suitable for the production of ethylene polymers having very high molecular weight. Thus a further object of the present invention is a process for polymerizing ethylene comprising contacting one or more of said olefins under polymerization conditions in the presence of the catalyst system described above.

Preferably the ethylene polymer obtainable with the catalyst system object of the present invention has a molecular weight Mw higher than 500,000; more preferably higher than 700,000; even more preferably higher than 1,000,000; still more preferably Mw can be higher than 1,300,000.

The following Examples are given for illustrative purpose and do not intend to limit the invention.

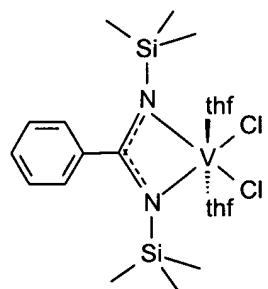
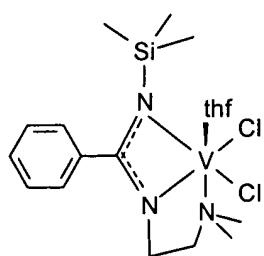
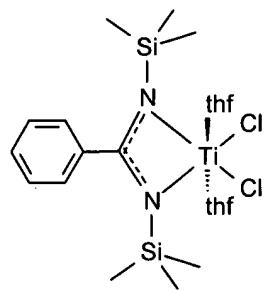
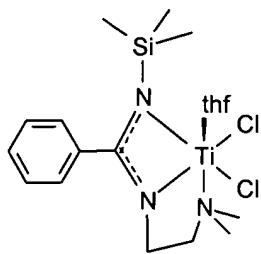
Materials and general procedures

All manipulations were performed under an argon atmosphere using A glove box (Braun MB-150 GI or LM-130) and Schlenk techniques. Solvents were distilled from Na (toluene) or Na/benzophenone (heptane) and freeze-thaw degassed twice before use.

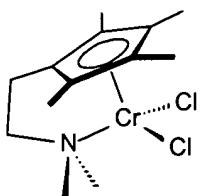
The vanadium aminidinate complexes **1** and **2** were prepared according to *Eur. J. Inorg. Chem.* **1998**, 1867. The analogous titanium amidinate complexes **3** and **4** were prepared as follows:

$[\{\text{PhC}(\text{NSiMe}_3)_2\}\text{TiCl}_2(\text{THF})_2]$ (**3**) was prepared by adding $[\text{PhC}(\text{NSiMe}_3)_2]\text{Li}(\text{THF})$ (1.1 g, 4.07 mmol) to a suspension of $\text{TiCl}_3(\text{THF})_3$ (1.50 g, 4.05 mmol) in THF (*ca.* 100 mL) cooled to -78 °C. The mixture was allowed to warm to room temperature while stirring, affording a dark green-brown solution. After stirring overnight, the volatiles were removed *in vacuo* and the residue was “stripped” twice (2 x 10 mL) with petroleum ether (40-70 distillates). The residue was then extracted with hot toluene (*ca.* 40 mL) and cooled to -30 °C, yielding **3** as dark-green needles (0.77 g, 37 %).

$[(\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{NMe}_2)\text{TiCl}_2(\text{THF})]$ (**4**) was prepared by adding $[(\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{NMe}_2)\text{Li}]$ (1.0 g, 3.69 mmol) to a suspension of $\text{TiCl}_3(\text{THF})_3$ (1.37 g, 3.70 mmol) in THF (*ca.* 100 mL) cooled to -78 °C. Further steps were as described for (**3**), yielding **4** as brown-green needles (0.54, 32 %).

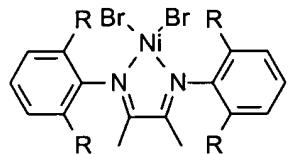
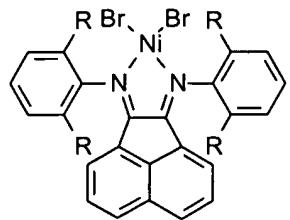
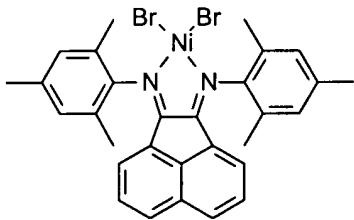
**1****2****3****4**

The chromium complex **5** [$\eta^1:\eta^5\text{-Me}_2\text{NCH}_2\text{CH}_2\text{C}_5\text{Me}_4\text{CrCl}_2$] was prepared according to A. Döring, J. Göhre, P.W. Jolly, B. Kryger, J. Rust, G.P.J. Verhovnik, *Organometallics* **2000**, *19*, 388.



5

The nickel complexes **6** - **9** (R=isopropyl) were prepared according to procedures reported in: L.J. Johnson, C.M. Killian, M. Brookhart, *J. Amer. Chem. Soc.* **1995**, *117*, 6414, and R.J. Maldanis, J.S. Wood, A. Chandrasekaran, M.D. Rausch, J.C.W. Chien, *J. Organometal. Chem.* **2002**, *645*, 158.

**6****7****8****9**

AlMe_3 (2M in hexane), AlEt_3 (25 wt-% solution in toluene) and $\text{Al}''\text{Oct}_3$ (25 wt-%, ca. 0.5M in hexanes) were obtained from Aldrich. Al^iBu_3 (1M solution in hexane) was purchased from Fluka.

Ethylene (3.5 grade supplied by Air Liquide) was purified by passing over columns of 4 \AA Molecular Sieves and BTS copper catalyst.

The Al and transition metal contents were determined by ICP / atomic absorption.

Surface area (BET) is determined according to BET methods (apparatus used: SORPTOMATIC 1800 from Carlo Erba).

The ethoxide content in the magnesium adducts was determined by GC analysis of the ethanol content of a solution obtained by dissolving 100 mg support in 5 mL *n*-BuOH containing a known quantity of *n*-PrOH as internal standard.

Preparation of partially dealcoholated adduct of formula MgCl₂·wUOH

The adduct MgCl₂·3EtOH was prepared according to the procedure described in Example 2 of US 4,399,054, operating at 3,000 rpm instead of at 10,000 rpm.

The adduct was partially dealcoholated by heating in a stream of nitrogen at temperatures increasing from 30°C. to 180°C.

Preparation of the support MgCl₂/AlQ_j(OEt)_{3-j}

10-50 mL *n*-heptane were added to 1-5 g of a spherical adduct of magnesium chloride and ethanol under argon and the mixture was cooled to 0 °C. A 25-28 wt-% solution of AlR₃ was then added gradually, over 5-10 min., to give a mol ratio AlR₃/EtOH = 2, the reaction being carried out in a standard Schlenk vessel equipped with a pressure release valve. The mixture was allowed to warm slowly to room temperature and the reaction was continued with occasional agitation for a further 1 day (AlMe₃), 2 days (AlEt₃), 3 days (AlⁱBu₃) or 4 days (Al["]Oct₃). The solid support was isolated by filtration, washed with heptane and petroleum ether (40-70) and then dried under a flow of argon and subsequently in vacuum. The compounds so obtained are reported in Table 1.

Preparation of the catalyst system - general procedure

A solution containing 1 µmol of the relevant transition metal complex (reported in Table 2) in toluene (1 mL) was added to 100 mg of support prepared as described above. The mixture was heated to 50 °C and kept at this temperature for 4 h. The toluene was then removed by decantation and the solid was reslurried in petroleum ether.

Polymerization - general procedure

Ethylene polymerization was carried out in a 1 L Premex autoclave equipped with a vortex stirrer. Petroleum ether (40-70, 450 mL) was introduced via a canulla. The reactor contents were stirred and heated to 50 °C. Triisobutylaluminium (TIBAL, 1 mmol) in petroleum ether (40-70, 10 mL) was introduced via the catalyst injection system. An ethylene overpressure of 0.5 MPa was applied and stirring continued for 5-10 min. A slurry of the immobilized catalyst (100 mg) in petroleum ether (40-70, 10 mL) was introduced through the catalyst injection system, which was then flushed with a further 50 mL petroleum ether (40-70). The ethylene pressure was increased to 1 MPa and kept constant for 2 h at a polymerization temperature of 50 °C, the stirrer speed being ca. 1000 rpm. After venting

the reactor, the polymer slurry was mixed with 20 mL of acidified methanol, 50 mL demineralised water and 10 mL HCl (10 %). The polymer was recovered by filtration, washed with water (3 x 200 mL) and ethanol (2 x 30 mL) and dried in vacuo overnight at 70 °C. The polymerization results are reported in Table 2.

Table 1. Composition of MgCl₂/AlR_n(OEt)_{3-n} supports

Reactants		Product		Overall Composition
Starting material	Al alkyl	Al, wt-%	OEt, wt.-%	
MgCl ₂ .1.1 EtOH	AlMe ₃	5.16	6.2	MgCl ₂ .0.22AlMe _{2.28} (OEt) _{0.72}
MgCl ₂ .1.1 EtOH	AlEt ₃	3.33	4.6	MgCl ₂ .0.14AlEt _{2.17} (OEt) _{0.83}
MgCl ₂ .1.1 EtOH	Al <i>i</i> Bu ₃	3.00	3.3	MgCl ₂ .0.13Al <i>i</i> Bu _{2.33} (OEt) _{0.67}
MgCl ₂ .1.1 EtOH	Al ⁿ Oct ₃	1.96	0.9	MgCl ₂ .0.09Al ⁿ Oct _{2.72} (OEt) _{0.28}
MgCl ₂ .2.1 EtOH	AlMe ₃	8.06	9.4	MgCl ₂ .0.39AlMe _{2.30} (OEt) _{0.70}
MgCl ₂ .2.1 EtOH	AlEt ₃	5.21	6.1	MgCl ₂ .0.24AlEt _{2.30} (OEt) _{0.70}
MgCl ₂ .2.1 EtOH	Al <i>i</i> Bu ₃	3.32	3.9	MgCl ₂ .0.15Al <i>i</i> Bu _{2.30} (OEt) _{0.70}
MgCl ₂ .2.1 EtOH	Al ⁿ Oct ₃	2.61	1.3	MgCl ₂ .0.13Al ⁿ Oct _{2.70} (OEt) _{0.30}

Table 2

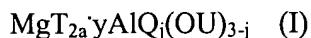
run	complex	magnesium adduct	activity kg/mol. bar.h	Mw	Mw/Mn
1	1	MgCl ₂ .0.24AlEt _{2.30} (OEt) _{0.70}	3120	762,000.	2.0
2	2	MgCl ₂ .0.24AlEt _{2.30} (OEt) _{0.70}	1490	747,000	2.0
3	3	MgCl ₂ .0.24AlEt _{2.30} (OEt) _{0.70}	2250	602,000	2.3
4	4	MgCl ₂ .0.24AlEt _{2.30} (OEt) _{0.70}	1920	611,000	2.3
5	5	MgCl ₂ .0.22AlMe _{2.28} (OEt) _{0.72}	1910	1,396,000	1.8
6	5	MgCl ₂ .0.14AlEt _{2.17} (OEt) _{0.83}	2690	1,560,000	1.9
7	5	MgCl ₂ .0.13Al ^t Bu _{2.33} (OEt) _{0.67}	1970	1,318,000	1.8
8	5	MgCl ₂ .0.09Al ⁿ Oct _{2.72} (OEt) _{0.28}	1880	1,451,000	1.8
9	5	MgCl ₂ .0.39AlMe _{2.30} (OEt) _{0.70}	1780	n.a.	n.a.
10	5	MgCl ₂ .0.24AlEt _{2.30} (OEt) _{0.70}	2530	n.a.	n.a.
11	5	MgCl ₂ .0.15Al ^t Bu _{2.30} (OEt) _{0.70}	1960	n.a.	n.a.
12	5	MgCl ₂ .0.13Al ⁿ Oct _{2.70} (OEt) _{0.30}	1170	n.a.	n.a.
13	6	MgCl ₂ .0.24AlEt _{2.30} (OEt) _{0.70}	1190	1,300,000	2.3
14	6	MgCl ₂ .0.24AlEt _{2.30} (OEt) _{0.70}	1162	n.a.	n.a.
15	7	MgCl ₂ .0.24AlEt _{2.30} (OEt) _{0.70}	4224	300,000.	2.7
16	8	MgCl ₂ .0.24AlEt _{2.30} (OEt) _{0.70}	1242	n.a	n.a.
17	8	MgCl ₂ .0.24AlEt _{2.30} (OEt) _{0.70}	1270	510,000	2.1
18	9	MgCl ₂ .0.24AlEt _{2.30} (OEt) _{0.70}	7158	290,000	2.9
19*	9	MgCl ₂ .0.24AlEt _{2.30} (OEt) _{0.70}	11416	n.a.	n.a.

*=(30 min. polymerization)

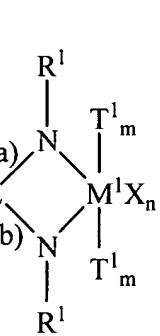
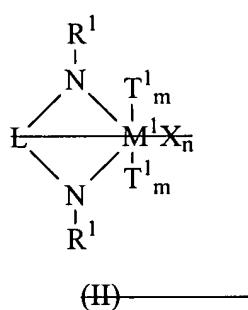
n.a.= not available

Abstract

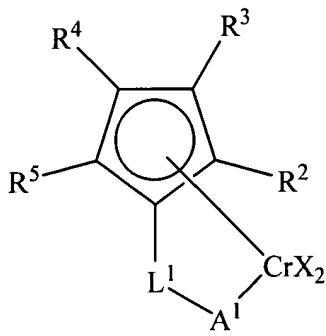
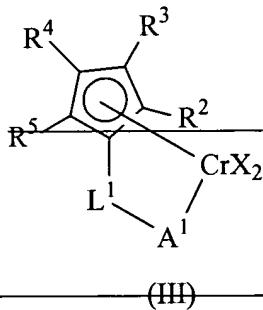
A supported catalyst system comprising the product obtainable by contacting an adduct of formula (I)



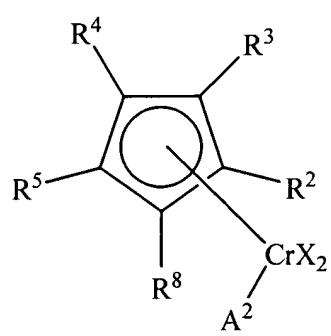
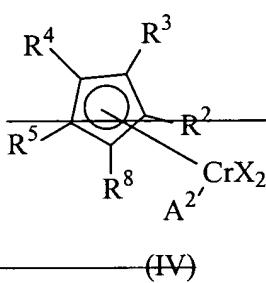
wherein T is chlorine, bromine, or iodine; U is a linear or branched C₁-C₁₀ alkyl radical, y ranges from 6.00 to 0.05; j ranges from 3 to 0.1; Q substituents, are hydrocarbon radicals containing from 1 to 20 carbon atoms; with at least one compound selected from the compounds of formula (II), (III) and (IV)



(II)



(III)



(IV)

wherein M¹ is a transition metal atom selected from Groups 3-11 of Periodical Table; each R¹, R², R³, R⁴, R⁵ and R⁸ is a hydrogen atom, a halogen atom or a hydrocarbon group; L and L¹ are divalent or trivalent hydrocarbon groups; T¹ is a Lewis base; A1 and A2 are oxygen sulfur or nitrogen containing groups and X is hydrogen halogen or hydrocarbon group.